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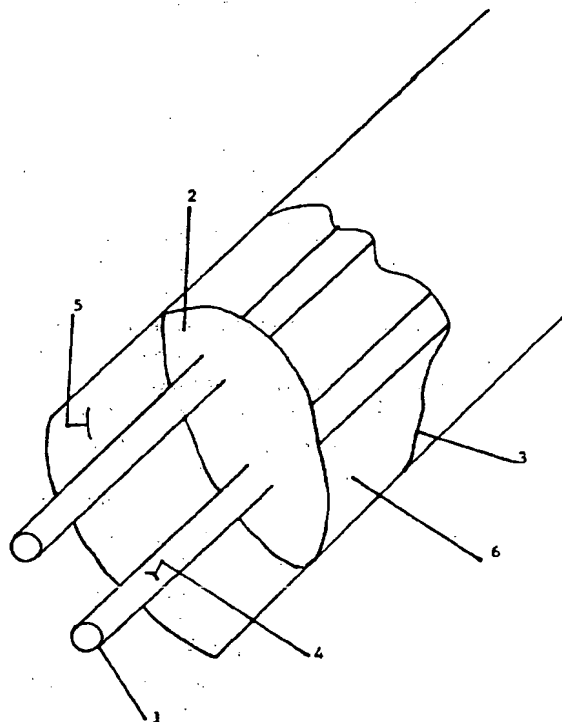
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54 **Insulating composition.**

57 An ethylene glycol composition containing a glycol-compatible welan gum having unique viscosity and thermal properties. The composition is especially suitable as an insulation material.

FIGURE 1



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The composition also aids in ballasting of pipe bundles. Conventional insulation materials such as extruded foams and insulation wrappings, which are low density materials, do not provide such stability.

With regard to temperature related stability, the composition is much more stable than kerosene based fluids, laminates and foams. The composition is also useful as a thickened de-icing and anti-icing fluid, especially for aircraft and other machinery that needs to be kept free of ice build-up in freezing weather.

In addition to the use described above, the thixotropic rheological properties of the composition make it suitable for use as an oil well insulating packer material, a ballast material, a non-petroleum based hydraulic material for motor actuating cylinders and a reservoir work over completion "kill" material.

Preferably, compositions of the present invention include those comprising weight ratios of glycol:glycol-compatible welan gum of between 100:1 and 300:1, more preferably 150:1 and 250:1, even more preferably 175:1 and 225:1 and even more preferably 180:1 and 220:1. Most preferably, the weight ratio is about 195:1.

More preferably, compositions of the present invention additionally comprise a metal sequestrant in an amount between 500 ppm and 2000 ppm, preferably 1250 ppm. A preferred sequestrant is EDTA.

Figure 1 shows a perspective cross-sectional view of a system for containing and transporting a fluid. The system comprises one or more subject fluid pipes 1 extending through and contacting a series of supports 2; carrier pipe 3 contacting supports 2, whereby the exterior surface or surfaces 4 of subject fluid pipe or pipes 1 oppose interior surface 5 of carrier pipe 3; and chamber 6 between exterior surface or surfaces 4 of subject fluid pipe 1 and interior surface 5 of carrier pipe 3.

In the system of the present invention, viscosified ethylene glycol containing glycol compatible welan gum, is introduced to chamber 6. The viscosified glycol's thixotropic rheological property makes it suitable, under shear stress, for introduction to the chamber as a pumpable liquid material. When the viscosified glycol substantially fills the chamber and is under minimal or no shear stress, it rests as a Bingham plastic. The material rests within carrier pipe 3 and surrounds subject fluid pipes 1, contacting supports 2 and surfaces 4 and 5.

The viscosified glycol is useful in a method for transporting a subject fluid through a lower temperature environment surrounding the subject fluid, wherein the subject fluid pipe, extending through a carrier pipe and forming a chamber between the exterior surface of the subject fluid pipe and the interior surface of the carrier pipe, is insulated from the lower temperature environment, which comprises introducing the viscosified glycol into the chamber.

The subject fluid for which the above described system is especially useful is oil obtained from undersea oil wells. Such oil, naturally having a temperature greater than that of the sea, is insulated from the lower sea temperature and retains its naturally elevated temperature as it flows through fluid pipe 1.

Kang et al., U.S. Patent No. 4,342,866 describes a procedure for making welan gum. Welan gum describes an industrial grade of a microbial polysaccharide produced by the growth of the *Alcaligenes* strain ATCC 31555 in a pure culture fermentation using carbohydrates as a carbon source. The product is recovered from the fermentation broth by precipitation with alcohol. Welan gum is a polysaccharide gum which comprises principally a heteropolysaccharide containing the neutral sugars D-glucose, D-glucuronic acid, L-rhamnose and L-mannose and glycosidically linked acetyl ester groups. The structure of this polysaccharide is described in Jansson PE, Lindberg B, and Widmalm G (1985) Carbohydrate Research 139, 217-223.

Preparation of glycol-compatible welan gum

Glycol-compatible welan gum is prepared by the procedure described in US 4,342,866. After fermentation, the broth is treated with sodium hypochlorite and calcium propionate followed by precipitation, drying and milling. A preferred process for preparing glycol-compatible welan gum useful in the present invention involves modification of the recovery process. The modification involves addition of sodium sulfate or potassium sulfate, preferably sodium sulfate, after-fermentation and prior to precipitation. Preferably, 0.1-1.0 wt. %, more preferably 0.3-0.7, and even more preferably 0.45 wt. % of sodium sulfate, is added to the fermentation broth.

Description of the strains used for producing glycol-compatible welan gum

A. Characteristics of Colonial Morphology

On nutrient agar, small yellow colonies appear in one day at at 30°C with the diameter reaching about 1.5 mm after 5 days' incubation. The colonies are round, smooth, convex, mucoid, and opaque. The yellow color becomes more deep and the texture of colonies becomes hard after prolonged incubation.

On YM agar, small mucoid yellow colonies appear in one day and the diameter reaches about 3 mm after 5 days' incubation. The colonies are round, smooth, convex, and opaque, but the top of the colonies are flat.

5	Kanamycin	30 µg
	Neomycin	30 µg
	Chlortetracycline	5 µg
	Novobiocin	30 µg
10	Erythromycin	15 µg
	Tetracycline	30 µg
	Gentamicin	10 µg
15	Carbenicillin	50 µg

and not susceptible to:

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	Penicillin	10 units
25	Streptomycin	10 µg
	Colistin	10 µg
	Polymyxin B	300 units

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E. Nutritional Characteristics

Organic growth factors are not required and ammonium salts serve as the sole nitrogen source. A total of 30 organic compounds are utilized as sole source of carbon and energy. Most carbohydrates are utilized.

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F. G + C Content of the DNA

No DNA analysis was performed.

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G. Identification by API System

The strain could not be identified by this system.

H. Identification

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The strain S-130 is a gram-negative aerobic rod-shaped organism. The mode of flagellation of the organism is mixed; polar and peritrichous flagella (possibly degenerate flagella) are seen. According to Bergey's Manual (8th Edition), such organisms belong as a member of the genus *Alcaligenes*.

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In general, carbohydrates (for example, glucose, fructose, maltose, sucrose, xylose, mannitol and the like) can be used either alone or in combination as sources of assimilable carbon in the nutrient medium. The exact quantity of the carbohydrate source or sources utilized in the medium depends in part upon the other ingredients of the medium but, in general, the amount of carbohydrate usually varies between about 2% and 4% by weight of the medium. Preferably 3% glucose is used. These carbon sources can be used individually, or several such carbon sources may be combined in the medium. In general, many proteinaceous materials may be used as nitrogen sources in the fermentation process. Suitable nitrogen sources include, for example, yeast hydrolysates, primary yeast, soybean meal, cottonseed flour, hydrolysates of casein, corn steep liquor, distiller's solubles or tomato paste and the like. The sources of nitrogen, either alone or in combination, are used in amounts ranging from about 0.05% to 0.4% by weight of the aqueous medium.

Among the nutrient inorganic salts which can be incorporated in the culture media are the customary salts capable of yielding sodium, potassium, ammonium, calcium, phosphate, sulfate, chloride, carbonate, and the like ions. Also included are trace metals such as cobalt, manganese, iron and magnesium.

It should be noted that the media described in the examples are merely illustrative of the wide variety of media which may be employed, and are not intended to be limitative.

As an alternative medium, S-130 may be grown under low Ca^{++} conditions, i.e., in deionized water, or some other aqueous system substantially free of Ca^{++} ions (i.e., less than about 4ppm Ca^{++} per 1% gum in the final fermentor broth).

The fermentation is carried out at temperatures ranging from about 25°C to 35°C; however, for optimum results it is preferable to conduct the fermentation at temperatures of from about 28°C to 32°C. The pH of the nutrient media for growing the *Alcaligenese* culture and producing the polysaccharide S-130 can vary from about 6 to 8, preferably 6.5 to 7.5.

Although the polysaccharide is produced by both surface and submerged culture, it is preferred to carry out the fermentation in the submerged state.

A small scale fermentation is conveniently carried out by inoculating a suitable nutrient medium with the culture, and after transfer to a production medium permitting the fermentation to proceed at a constant temperature of about 30°C on a shaker for several days.

The fermentation is initiated in a sterilized flask of medium via one or more stages of seed development. The nutrient medium for the seed stage may be any suitable combination of carbon and nitrogen sources. The seed flask is shaken in a constant temperature chamber at about 30°C for 1-2 days, or until growth is satisfactory, and some of the resulting growth is used to inoculate either a second stage seed or the production medium. Intermediate stage seed flasks, when used, are developed in essentially the same manner; that is, part of the contents of the flask from the last seed stage are used to inoculate the production medium. The inoculated flasks are shaken at a constant temperature for several days, and at the end of the incubation period the contents of the flasks are recovered by precipitation with a suitable alcohol such as isopropanol.

For large scale work, it is preferable to conduct the fermentation in suitable tanks provided with an agitator and a means of aerating the fermentation medium. According to this method, the nutrient medium is made up in the tank and sterilized by heating at temperatures of up to about 121°C. Upon cooling, the sterilized medium is inoculated with a previously grown seed of the producing culture, and the fermentation is permitted to proceed for a period of time as, for example, from 2 to 4 days while agitating and/or aerating the nutrient medium and maintaining the temperature at about 30°C. This method of producing the heteropolysaccharide is particularly suited for the preparation of large quantities.

Post-fermentation

Preferably, after fermentation, and prior to product recovery from fermentation medium, potassium sulfate or sodium sulfate is added to the fermentation medium. Addition of about 0.1-1.0 wt. % of the broth of potassium sulfate or sodium sulfate is critical for obtaining glycol-compatible welan gum. The glycol-compatible welan gum so obtained possesses hydrating properties essential for forming the insulation fluid of the present invention.

Analysis

Glucuronic acid was identified by using the method of Bhatti et al., *Biochim. Biophys. Acta* 22 (1970) 339-347. Absolute configurations of the sugars were determined by the methods devised by Gerwig et al., *Carbohydrate Research* 77 (1979) 1-7, and by Leontein et al., *Carbohydrate Research* 62 (1978) 359-362.

Methylation analyses were performed essentially as described in Jansson et al., *Chem. Common. Univ. Stockholm*, 8 (1976) 1-75. Methylated polymers were recovered by dialysis against water, followed by freeze-drying. Low-molecular-weight products were recovered by reversed phase chromatography on Sep-Pak C₁₈.

TABLE II

METHYLATION ANALYSIS OF THE POLYSACCHARIDE
AND SOME DEGRADATION PRODUCTS^a

Sugar ^b	T ^c	Mole %				
		A	B	C	D	E
1,2,3,5-Rhammitol	0.38				13	22
2,3,4-Rha	0.59	12	7	16		
2,3-Rha	0.94	26	21	18		
2,3,4,6-Glc	1.00				54	36
2,3,4,6-Man	1.00	10	7	19		5
2,4,6-Glc	1.67	26	23	43 ^d		
2,3,6-Glc	1.92				33	34
2,6-Glc	2.79	26	23	4		3
2,3-Glc	3.56		19			

^aKey: A, methylated polysaccharide; B, methylated and carboxyl-reduced polysaccharide; C, uronic acid-degraded polysaccharide; D, acidic tetrasaccharide; E, acidic penta- and tetra-saccharide.

^b2,3,4-Rha=2,3,4-tri-O-methyl-L-rhamnose, etc. ^cRetention time of the corresponding alditol acetate, relative to 1,5-di-O-acetyl-2,3,4,6-tetra-O-methyl-D-glucitol on an SP-1000 glass-capillary column at 200°C. ^d>90% Trideuteriomethyl at 0-4.

In order to determine the sequence of the sugar residues, the glycol-compatible welan gum polysaccharide was subjected to a uronic acid-degradation (Lindberg et al. *Carbohydrate Research* 28 (1973) 351-357 and Aspinall et al. *Carbohydrate Research* 57 (1977) c23-c26). The fully methylated polysaccharide was treated with sodium methylsulfinylmethanide in dimethyl sulfoxide, methylated (using trideuteriomethyl iodide), and hydrolyzed, and the mixture of methylated sugars was analyzed (Table II, column C). 2,6-di-O-methyl-4-O-trideuteriomethyl-D-glucose was derived from the branching D-glucopyranosyl residue, the 4-position of which was liberated on degradation of the uronic acid. The 3-substituted D-glucopyranosyl residue linked to O-4 of the uronic acid was released by β -elimination and further degraded by β -elimination, with release of the 4-substituted L-rhamnopyranosyl residue. A considerable part of this residue was also degraded.

EXAMPLE 1

Fermentation Procedure for Producing Glycol-Compatible Welan Gum

A. Culture Maintenance

The unnamed *Alcaligenes* organism, ATCC 31555, grows quite well on NA agar, with good colonial morphology. The incubation temperature is 30°C. The organism produces a yellow pigment.

EXAMPLE 2

Insulating Composition

5 2 lbs of glycol-compatible welan gum was combined with 390 lbs ethylene glycol. 1250 ppm EDTA is added as a sequestrant. The composition was hydrated on an Oster blender stirring at 10,000+ rpm for 20 minutes. The composition is non-polluting to marine life up to 200,000 ppm.

The composition was tested for thermal conductivity and shown to be superior to several alternative insulating materials:

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Thermal Conductivity(Watts/m)

15	Gelled Insulating	
	Composition (Example 2)	91
	Liquid Ethylene glycol	4022
	Nitrogen @ atm. pressure	162
20	Nitrogen @ 10 atm.	436
	Nitrogen @ 30 atm.	729

EXAMPLES 3-10

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Following the procedure described in Example 2, the following compositions, containing two pounds glycol-compatible welan gum, 1250 ppm EDTA and various amounts of ethylene glycol, are prepared.

	<u>Example No.</u>	<u>Ethylene Glycol (lbs)</u>
30	3	200
	4	300
	5	350
35	6	360
	7	440
	8	450
	9	500
40	10	600

The compositions described in Example 3-10 showed varying degrees of thixotropic properties of the composition described in Example 2. The composition in Example 3 retains a high degree of viscosity, and although its thermal conductivity is suitable, it is less convenient to manipulate for certain purposes, such as for the oil insulation purpose described above. The composition of Example 10 is easier to manipulate than the composition described in Example 2, but its thermal conductivity is more like pure ethylene glycol.

EXAMPLE 11

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Another Fermentation Procedure for Producing Glycol-Compatible Welan Gum

A. Culture Maintenance

55 The unnamed *Alcaligenes* organism, ATCC 31555 grows quite well on nutrient agar. The incubation temperature is 30°C. the organism produces a yellow pigment.

LVT, has a viscosity greater than about 2,500 cP.

2. A composition of Claim 1 which further comprises a chelating agent.
- 5 3. A composition of Claim 1 wherein the glycol and glycol-compatible welan gum are present in a weight ratio of between about 100:1 and 300:1.
4. A composition of Claim 3 wherein the ratio is between about 150:1 and 250:1.
- 10 5. A composition of Claim 4 wherein the ratio is between about 175:1 and 225:1.
6. A composition of Claim 5 wherein the ratio is between about 180:1 and 220:1.
7. A composition of Claim 6 wherein the ratio is about 195:1.
- 15 8. A composition of Claim 2 wherein the sequestrant is EDTA present in an amount of between about 500 ppm and 2000 ppm.
- 20 9. A method for transporting a subject fluid through a lower temperature environment surrounding the subject fluid, wherein a subject fluid pipe, extending through a carrier pipe and forming a chamber between the exterior surface of the subject fluid pipe and the interior surface of the carrier pipe, is insulated from the lower temperature environment which comprises introducing a composition of Claim 1 into the chamber.

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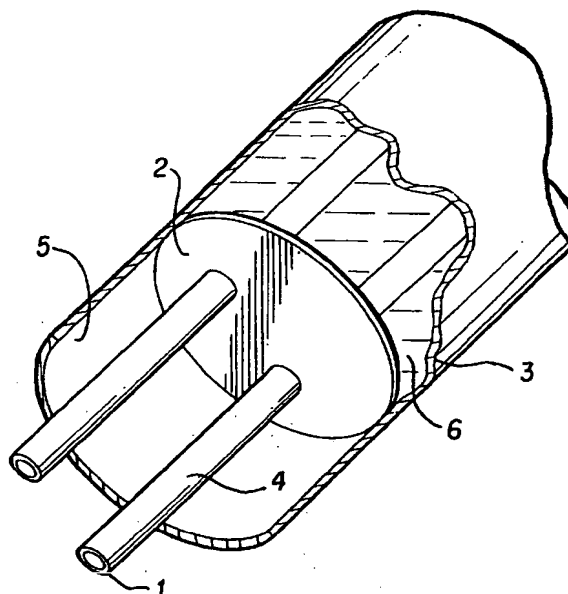


FIG. 1